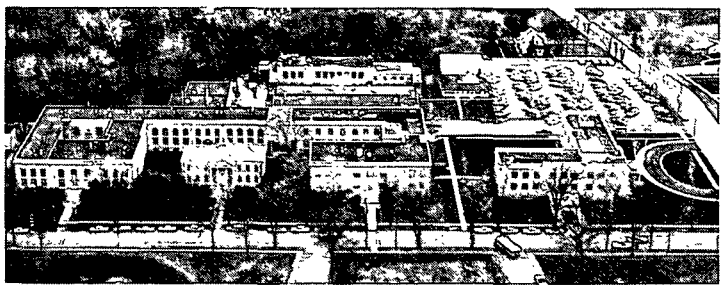

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THE EFFECT OF NITROGEN DIOXIDE PRETREATMENTS ON SOME PROPERTIES OF OXYGEN-BLEACHED KRAFT PULPS

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ABSTRACT

Pine kraft pulps were reacted with nitrogen oxides and bleached with oxygen at different alkalinity levels. Lignin was not removed by the pretreatments used here, and cellulose suffered viscosity losses. Lignin removal was not enhanced by oxygen bleaching, but cellulose was less degraded than in the corresponding controls. Zero-span tensile tests of the pretreated bleached pulps showed them to be stronger than the controls. The darker color of the pretreated pulps compared to the controls was partially alleviated by a posttreatment with sodium dithionite. The beneficial effect of nitrogen oxide pretreatments on cellulose viscosity was attributed to the more electronegative nature of lignin radicals produced by the oxygen stage. The effect of other lignin deactivating substituents is also discussed.

INTRODUCTION

The need to improve the specificity of oxygen for lignin during bleaching has triggered much research in many laboratories. The effect of numerous antioxidant additives on this system has been investigated at the Institute with limited success (1). We concluded that the complex nature of wood and pulp rendered the approach impractical and that a better approach would involve improving the suspected antioxidant character of lignin. This might be achieved by increasing the nucleophilicity of lignin and its degradation products.

The effect of nitrogen oxides on pulp has been investigated with some success by Yethon (2), Samuelson (3) and Patt (4) and several others. We suspected that this behavior might be related to changes in the autoxidative behavior of lignin. This paper describes attempts to understand the reasons for the improved selectivity of O_2 for lignin pretreated with NO_2.

EXPERIMENTAL

The nitrogen dioxide ($2NO_2 \rightleftharpoons N_2O_4$) used in these experiments was provided as a liquid by a commercial distributor. Moisture in one cylinder resulted in the presence of a mixture of nitrogen oxides which were detected by physical characteristics and mass spectroscopy. The second cylinder contained relatively pure NO_2. Both gases were used in these experiments, and no significant differences in their chemical reactions with pulp were observed.

The equipment used in this investigation was very similar to that described by Samuelson (3) and is shown in Fig. 1. Calculated quantities of liquid NO_2 at -10°C were flashed into a 3 L flask containing 40 g of a commercial southern pine kraft pulp (30 kappa, 28% consistency, fluffed at 22°C, ~ 0.2 atmospheric pressure). Three flushes of O_2 were employed to sweep all oxide fumes into the reaction flask and convert NO to NO_2. Kraft eucalyptus pulp was also employed. The pulps turned reddish brown almost immediately, and after 10 minutes 500 mL water was added to the flask. It was shaken for 5 minutes until all gaseous oxides had been dissolved. The pulp was washed twice with 3 L distilled water to remove water solubles. A sample was removed for chemical characterization, and the pulps were prepared for oxygen bleaching.

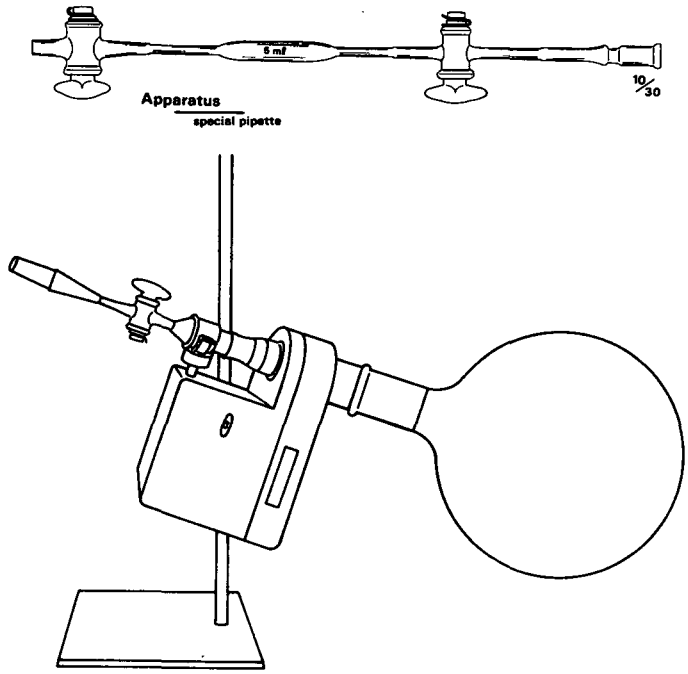

Fig. 1 Apparatus used to pretreat pulp with nitrogen oxides.

Control reactions using concentrated nitric acid containing a calculated amount of NO_2 were fluffed into the pulp. The pulps were treated and worked up in the same manner as the NO_2 treated pulps.

Pulps for O_2 bleaching were fluffed with a calculated quantity of NaOH dissolved in sufficient water to make pulp at 25% consistency. Seven pretreated pulps were simultaneously bleached with oxygen in a multistage reactor. The conditions were 120°C, 100 psi O_2, 25% consistency, 1% magnesium sulfate, for 30 minutes using 2, 4, or 5% NaOH based on pulp.

Following isolation, the pulps were analyzed for yield, K number (5), viscosity (6), brightness (7), and zero-span tensile strength (8) while some pulps were examined using FT-IR. For comparative purposes, some cuene viscosities were converted to apparent degrees of polymerization (9) and some permanganate numbers converted to kappa numbers for comparison with other values in the literature.

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Other experiments were conducted employing posttreatment reducing agents such as SO_2, $NaBH_4$, and $Na_2S_2O_4$, (24-36 hours at 5°C, concentrations adjusted to ensure excess, the last two over N_2, washed with water to constant pH). These pulps were also bleached with oxygen.

RESULTS

Chemical Considerations

Kraft pulp turned dark (reddish brown) when reacted with nitrogen oxides, whereas the nitric acid pretreated pulp did not do so. FT-IR analysis confirmed the presence of nitro groups demonstrated by others (10). The plot in Fig. 2 shows that no lignin was removed by this treatment, nor was lignin removed by the pretreatment with nitric acid. Patt (4) demonstrated lignin could be removed at this stage by suitable alkaline treatments. The small effect of nitrogen dioxide pretreatment on lignin removal (after bleaching with oxygen using 2% NaOH) diminished with increased alkali (4 and 6%) in the oxygen stage and where tested, the effect of nitric acid on lignin removal was identical to that of the corresponding oxide. Little obvious difference (except for color) exists between the action of NO_2 and HNO_3 on lignin behavior as a result of oxygen bleaching.

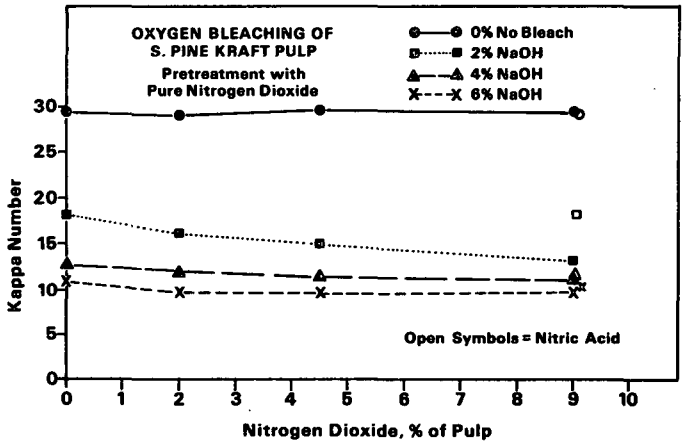

Fig. 2 The effect of nitrogen oxide pretreatments on the kappa content of pine kraft pulps bleached with oxygen at different alkalinities.

The effect of NO_2 on cellulose viscosity (without oxygen bleaching) is harmful and equal to that caused by nitric acid (Fig. 3). The degradation in both cases is probably hydrolytic in nature, and the limiting viscosity loss at high degrees of NO_2 application is probably a function of lignin accessibility to the gas.

The viscosity of the cellulose component of the NO_2 pretreated kraft pulp after oxygen bleaching is greater than that of the controls and of the corresponding HNO_3 pretreated pulp. The viscosity resulting from the use of only 2% alkali on the pulp shows little loss compared to the unbleached pretreated pulp. This suggests that oxygen bleaching using 2% NaOH has not degraded this cellulose at all! A relative stabilization of cellulose is achieved in all cases which is greater than that of the pulp which had not been pretreated. Increased degradation does occur at higher levels of alkali application during the bleach, but in all instances the resulting viscosity is always greater than either the control or the HNO_3 pretreated pulps.

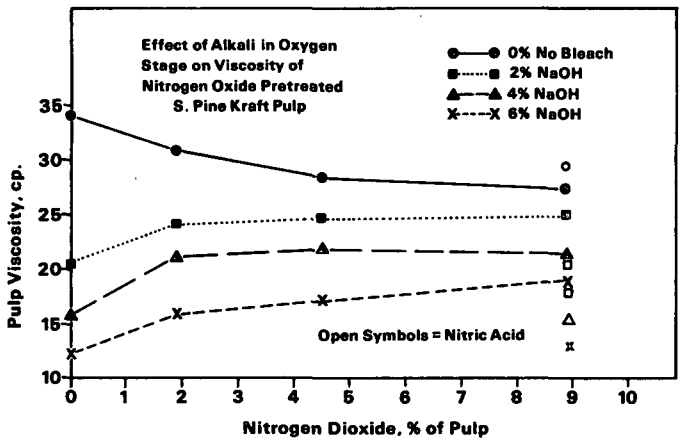

Fig. 3 The effect of nitrogen oxide pretreatments on the viscosity of pine kraft pulps bleached with oxygen at different alkalinities.

The effect of nitrogen dioxide pretreatment on pulp brightness after bleaching with oxygen using increasing amounts of applied alkali is shown in Fig. 4. Brightness is increased by increasing the severity of the bleach, but in no instance was it possible to bleach the pretreated pulps to the same brightness level as the bleached controls. This relative behavior is unchanged by heat aging. The pretreatments with nitric acid did not have such an adverse effect on brightness after oxygen bleaching.

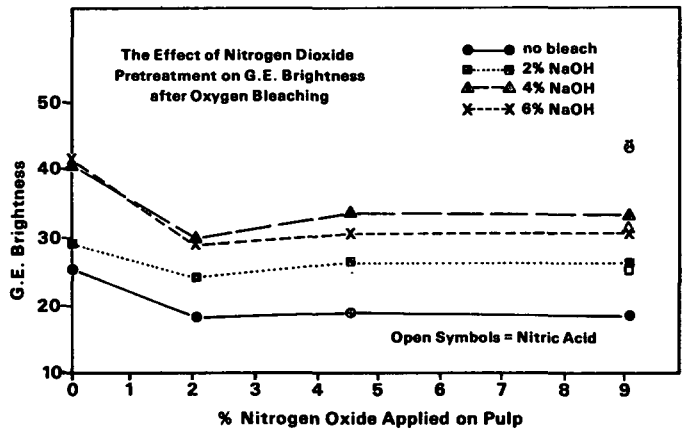

Fig. 4 The effect of nitrogen oxide pretreatments on the G.E. brightness of pine kraft pulps bleached with oxygen at different alkalinities.

Both lignin derivatives (from NO_2 and HNO_3) are removed by oxygen from pulp to similar extents, suggesting similar delignifying reactions. However, their different colors before and after oxygen bleaching suggest the presence of different functional groups which are not responsible for lignin removal. It has been shown that pretreated lignins

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can be removed from such pulps by suitable means before oxygen bleaching if desired (4). This chemical difference is attributed to the presence of nitro groups which enhance the reactivity of nitrated phenolate ions to oxygen (11).

The dark color of NO_2 pretreated pulps could be lightened with reducing bleaches such as SO_2, $Na_2S_2O_4$ and $NaBH_4$. In other experiments, only in the case of $Na_2S_2O_4$ posttreatment of the pretreated pulp was the pulp brightness significantly improved after subsequent oxygen bleaching. The response of the $NaBH_4$ posttreatment pulp to oxygen is shown in Fig. 5. The reductive treatment did not improve the DP of the cellulose over that of the control, nor did it improve the response of the HNO_3 pretreated pulp to oxygen, although delignification remained the same. The lower DP of the borax preextracted pulp probably reflects degradation in the alkaline medium. Therefore the use of NO_2 does not introduce carbonyl (ketonic) groups into cellulose, and this reinforces hydrolysis or oxidative cleavage as the primary cause of cellulose degradation during the pretreatment stage.

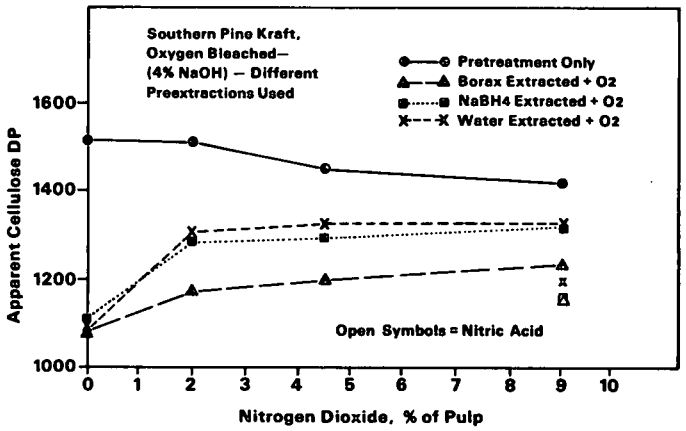

Fig. 5 The effect of $NaBH_4$ after nitrogen oxide pretreatments on the apparent cellulose DP of pine kraft pulps bleached with oxygen using 4% NaOH.

Physical Effects

Zero-span measurements are often taken as a first approximation of the potential strength of a papermaking fiber. The zero-span tensile tests of the pulps pretreated with impure NO_2 shown in Fig. 6 indicate that some fiber strength is lost as a result of pretreatment alone. This loss of strength is probably a result of the more bulky nitrated lignin inhibiting stress distributions during testing. The recovery of strength after oxygen bleaching might be due to better exposure of bonding sites and stress distribution as a result of lignin removal.

The effect of pretreatment of pulp with pure NO_2 on zero-span strength before oxygen bleaching is not as apparent, but it does indicate a maximum benefit using 4.5% NO_2 on pulp. If the result is not shown to be a testing problem, it might be conjectured to arise from degradative differences between the two pretreating agents.

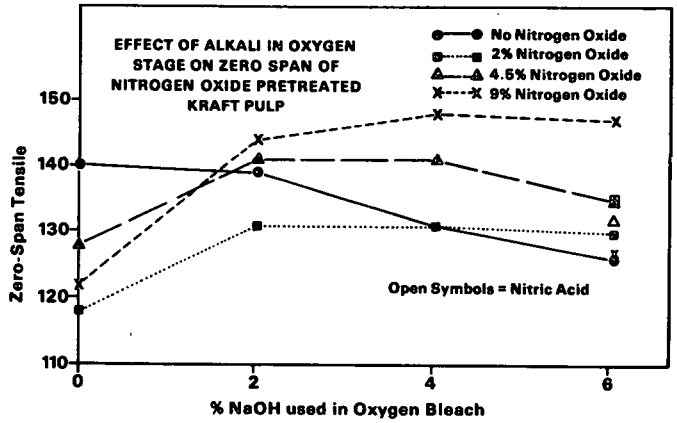

Fig. 6 The effect of nitrogen oxide pretreatments on the zero-span tensile strength of pine kraft pulps bleached with oxygen at different alkalinities.

DISCUSSION

These results can be explained by assuming that the hydrolytic degradations of moist cellulose by equivalent quantities of NO_2 and HNO_3 are very similar. On the other hand, it is likely that the lignins have been modified in different manners, since their colors and alkali solubilities are different (although they are removed by oxygen to similar extents). The functional groups associated with the reddish brown color are not necessarily those responsible for lignin removal but may reflect changes in lignin structure necessary for cellulose stabilization.

Cellulose in pulps pretreated with HNO_3 is less stable toward oxygen than is cellulose in pulps pretreated with NO_2 although their initial viscosities are almost identical. We suspect that the hydrolytic degradation wrought by these two reagents is identical and that the subsequent difference in cellulose behavior is caused by altered bleaching intermediates derived from lignin. General schemes for the radical reactions that occur during oxygen bleaching are illustrated in the literature by diagrams similar to Fig. 7. Because of their very short life-times in antagonistic environments (12), oxygen radicals derived from the interaction of phenolate ions with oxygen are probably not solely responsible for much cellulose degradation. Lignin intermediates, especially soluble fragments (organic radicals), produced by this reaction are stabilized by resonance and might be responsible for much additional delignification, as well as for cellulose degradation.

The introduction of nitro groups into aromatic nuclei increases their electronegativity (11,13). If this is true for lignin, then it indicates that the nitrated radicals (or other intermediates) derived from lignin are still able to assist in delignification. Since carbohydrates are degraded by an electrophilic attack (14), their degradation will be lessened because of the greater electronegativity of lignin fragments, which is what we observe. These factors influence both ionic and radical mechanisms; we feel the accumulated evidence of the last 2 decades favors a radical approach (15).

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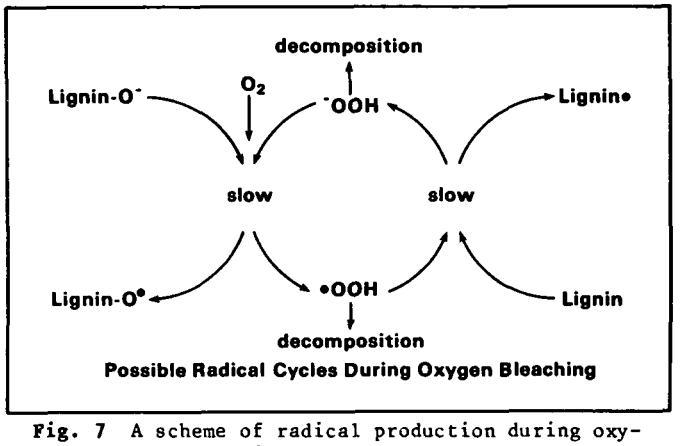

Fig. 7 A scheme of radical production during oxygen bleaching.

Other useful reagents capable of causing this chemical alteration of aromatic compounds are halogens, carboxyl, and sulfonic acid groups. Nitro groups and most other substituents activate all positions of an aromatic ring by electron withdrawal and deactivate the o and p positions especially by resonance stabilization. Halogens on the other hand, are o and p directing (activating), but they strongly deactivate rings to electrophilic substitution by an electron withdrawal effect. They should modify lignin differently than the others but nevertheless have a stabilizing effect on cellulose.

The plots in Fig. 8 taken from data of Lachenal and de Choudens (16) show the similar effects of chlorine and NO_2 pretreatments before oxygen bleaching on cellulose viscosity. It cannot be determined which gives better benefits until all experimental parameters are understood. Arguments can be made for the potential superiority of halogens. Bromine should be the least effective of the halogens while fluorine derivatives (if possible) should be the most effective. Obviously such organic chemistry considerations dictate numerous bleaching manipulations [such as pretreatments with peroxyacetic acid (1)] which can lead to additional novel pretreating concepts.

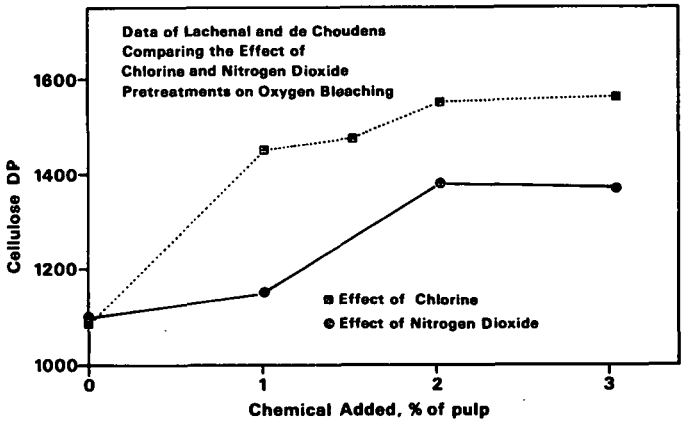

Fig. 8 A plot of the data of Lachenal and de Choudens comparing the effect of chlorine and nitrogen dioxide pretreatments on oxygen bleaching.

CONCLUSIONS

Lignin is altered by NO_2 pretreatments but not removed from pulp under the conditions used here. The carbohydrates are hydrolyzed but not significantly oxidized by the treatments. This cellulose is more stable to oxygen-alkali degradation than that in nontreated pulp or that in HNO_3 pretreated pulp. It is postulated that the more electronegative lignin and lignin fragments produced by reaction with NO_2 are not able to degrade cellulose as do more electropositive lignin derivatives. Radical mechanisms are favored. This rationalization also explains the behavior of certain chlorine and ozone pretreatments (16) and peroxy acids on cellulose stability, and it is likely that other electron withdrawing groups or manipulations will do the same. The physical constraints of pulp presently limit the effectiveness of pretreatments.

REFERENCES

1. Thompson, N. S., unpublished research, The Institute of Paper Chemistry, 1985.

2. Yethon, A. E., Can. pat. 1,045,759(1974); 1,070,909(1976).

3. Abrahamson, K., Lowendahl, L., and Samuelson, O., Svensk Papperstid. 84:R152(1981).

4. Patt, R. Application of nitrogen dioxide and ozone in the prebleaching of kraft and sulfite pulps. International Pulp Bleaching Conf., Tech. Sect. CPPA and TAPPI, Quebec City, June 18-21, 1985.

5. TAPPI Standard 214 m.

6. TAPPI Standard T23 su-66.

7. TAPPI Standard T217 m, T452 m.

8. TAPPI Standard T231 m.

9. TAPPI Data Sheet 113C, Dec., 1950.

10. Samuelson, O. and Sjoberg, L. A., Svensk Papperstid. 85:R69(1982).

11. Fessenden, R. J. and Fessenden, J. S., Organic Chemistry, Willard Grant Press, Boston, Mass., 1979.

12. Singh, A., Can. J. Physiol. Pharm. 60(11):1330 (1982).

13. Kodsachia, O., Wang, L. K., and Patt, R., Papier 38(11):517(1984).

14. Sinkey, J. D. and Thompson, N. S., Paperi Puu 56(5):473(1974).

15. Samuelson, O., Pure & Applied Chem. 55(4):695 (1983).

16. Lachenal, D. and de Choudens, C. High efficiency oxygen and peroxide delignification. TAPPI Oxygen Delignification Symp. (San Francisco) Notes, Nov. 15-16, 1984:87-89.

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